Products and SOA Formation From the NO_3 Radical-Initiated Oxidation of α-Pinene

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INTRODUCTION

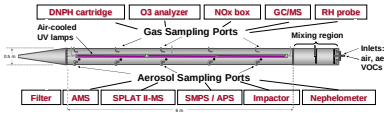
α-Pinene (AP) is known to react with O_3, OH and NO_3 radicals, leading to the formation of secondary organic aerosols (SOA). While particle formation and growth from the NO_3 radical reaction with α-pinene have been reported by a number of groups,[1-4] as have the gas phase products, little is known about the chemical composition of the particles.

GOALS

- To study the chemical composition of particles formed from NO_3 + α-pinene using two different sources of NO_3 radicals.
- To study the effect of $[NO_2]/[O_3]$ on secondary organic aerosol (SOA) formation from the NO_3 radical oxidation of α-pinene.

EXPERIMENTAL METHODS

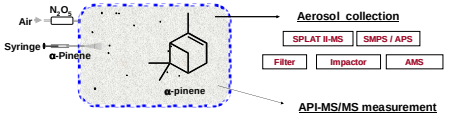
(1) Flow tube experiments using O_3+NO_2 as the NO_3 source



- Particles collected on quartz filters (total sample air volume 300-600 L) were extracted with acetonitrile and analyzed by GC-MS, ESI-MS (-), APCI-MS (+), HPLC-MS and HPLC-UV.
- Particles impacted on ZnSe windows (impactors, total sample air volume 540-1080 L) were analyzed using FTIR.

$[NO_2]$ from 0 to 6.3 ppm , $[O_3]$ = 1.6 ppm and [AP] = 1 ppm

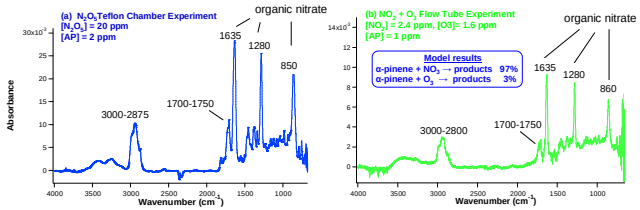
(2) Static chamber experiments using N_2O_5 as the NO_3 source



$[N_2O_5]$ from 1 ppm to 20 ppm and [AP] from 1.4 to 2 ppm

CHEMICAL CHARACTERIZATION OF THE PARTICLES: EVIDENCE OF PARTICULATE ORGANIC NITRATES

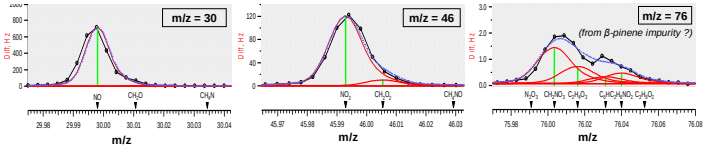
FTIR spectra of impacted particles on ZnSe windows (50% cut off point, 1.0 μm)



- N_2O_5 and NO_2+O_3 experiments both show 3 characteristic IR bands corresponding to organic nitrates (1630, 1280 and 860 cm^{-1})[3-4] as well as carbonyl compounds (1700-1750 cm^{-1}).

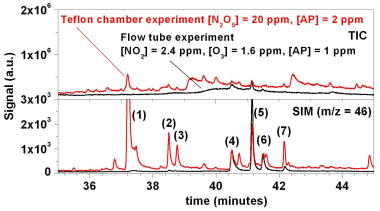
High-resolution AMS data ($T_{vaporizer}$ = 600°C)

$[NO_2]$ = 2.4 ppm / $[O_3]$ = 1.6 ppm / [AP] = 1 ppm



- Organic nitrate signature: NO^+/NO_2^+ ~6 to 9 compared to 3.2 for NH_4NO_3 and 65 for $NaNO_3$ [5].
- Observation of specific fragments such as m/z = 76 ($CH_2NO_3^+$) from NO_3 reaction with biogenic compounds (β-pinene, limonene, Δ- carene, isoprene (and α-pinene ?))

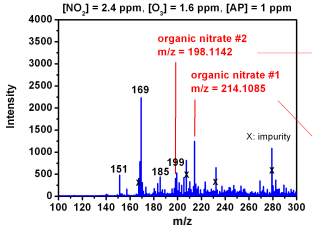
GC-MS chromatogram from quartz filter extract

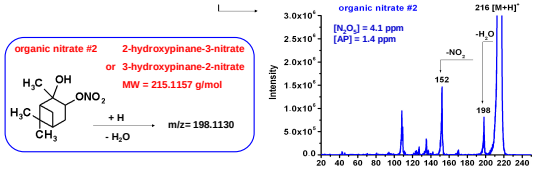


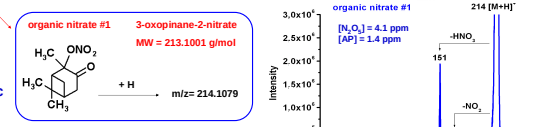
- Up to 7 organic nitrates were found in NO_3 radical-initiated experiments.

- NO_3 radical-initiated chemistry forms organic nitrates as well as a variety of other products.
- Carbonyl compounds observed (GC/MS, APCI-MS(+), API-MS/MS(+)): pinonaldehyde, hydroxy-pinonaldehyde, campholene aldehyde, norpinonaldehyde.
- Carboxylic acids observed (GC/MS, ESI-MS(-)): pinonic acid, pinic acid and ketopinonic acid.
- Pinonaldehyde was also found in the gas phase (confirmed by DNPH measurement) as well as formaldehyde, acetone, formic acid and acetic acid.

APCI-MS (+) spectra from quartz filter extract







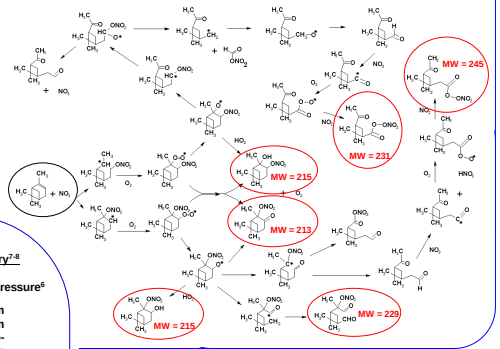
- The use of high-resolution mass spectrometric methods as well as MS/MS scan mode allow structural identification of organic nitrates.

API-MS/MS (+) spectra from Teflon chamber – product ions mode scan

API-MS/MS (+) and APCI-MS (+) Identification of several potential organic nitrates and oxygenated compounds

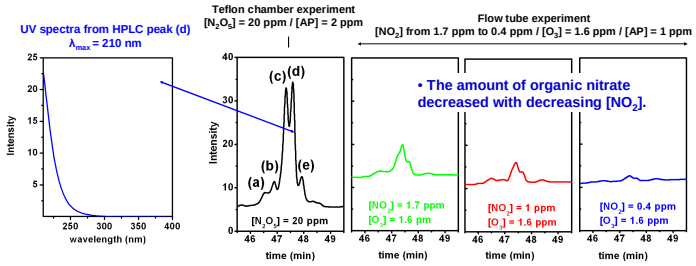
MW		Compound	Estimated vapor pressure[6]
213		3-oxopinane-2-nitrate	$P_{L,i}^0$ = 1.7 x 10^{-6} atm
215		3-hydroxypinane-2-nitrate or 2-hydroxypinane-3-nitrate	$P_{L,i}^0$ = 8.4 x 10^{-6} atm
245		(3-acetyl-2,2-dimethylcyclobutyl)acetyl peroxynitrate (pinonaldehyde-PAN)	$P_{L,i}^0$ = 1.3 x 10^{-5} atm
231		(3-acetyl-2,2-dimethylcyclobutyl)formyl peroxynitrate (norpinonaldehyde-PAN)	$P_{L,i}^0$ = 3.7 x 10^{-6} atm
229		2-(3-formyl-2,2-dimethylcyclobutyl)-2-nitroxypropanal	$P_{L,i}^0$ = 2.9 x 10^{-8} atm
169 (+151)		pinonaldehyde	$P_{L,i}^0$ = 1.3 x 10^{-5} atm
185		hydroxypinonaldehyde	$P_{L,i}^0$ = 7.6 x 10^{-8} atm
	or	pinonic acid	$P_{L,i}^0$ = 7.7 x 10^{-8} atm
199		7-ketopinonic acid	$P_{L,i}^0$ = 3.4 x 10^{-9} atm
	or	4-ketopinonic acid	$P_{L,i}^0$ = 8.9 x 10^{-9} atm

Proposed mechanism



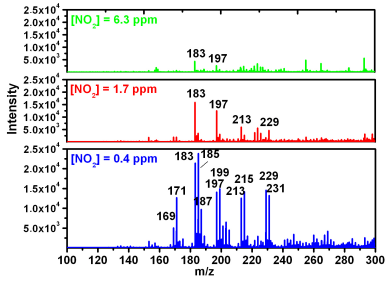
INFLUENCE OF $[NO_2]/[O_3]$ ON THE NO_3 RADICAL OXIDATION OF α-PINENE

HPLC-UV chromatogram from quartz filter extract (λ = 210 nm)



- The amount of organic nitrate decreased with decreasing $[NO_2]$.

ESI-MS (-) spectra from quartz fiber filter extract



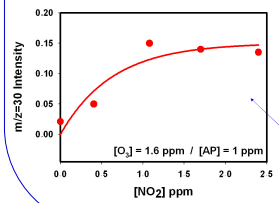
Organic compounds identified in the particles due to O_3 chemistry[7-8]

m/z		Compound	Estimated vapor pressure[6]
169 (+229)		pinalic acid	$P_{L,i}^0$ = 8.1 x 10^{-8} atm
	or	norpinonic acid	$P_{L,i}^0$ = 2.1 x 10^{-7} atm
171 (+231)		"pinolic acid" (3-(2-hydroxyethyl)-2,2-dimethylcyclo-butane carboxylic acid)	$P_{L,i}^0$ = 1.1 x 10^{-8} atm
	or	norpinic acid	$P_{L,i}^0$ = 1.3 x 10^{-9} atm
183*		pinonic acid	$P_{L,i}^0$ = 7.7 x 10^{-8} atm
	or	hydroxypinonaldehyde	$P_{L,i}^0$ = 7.6 x 10^{-6} atm
185		pinic acid	$P_{L,i}^0$ = 4.8 x 10^{-10} atm
197*		7-ketopinonic acid	$P_{L,i}^0$ = 3.4 x 10^{-9} atm
	or	4-ketopinonic acid	$P_{L,i}^0$ = 8.9 x 10^{-9} atm
199		hydroxypinonic acid	$P_{L,i}^0$ = 4.5 x 10^{-10} atm

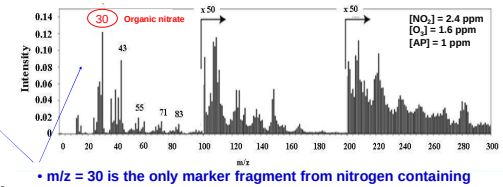
* (also formed in the NO_3 radical initiated oxidation of α-pinene)

- As $[NO_2]$ decreased, while the amount of organic nitrate decreased, additional products (carboxylic acids) with very low vapor pressure increased in concentration as illustrated by the ESI-MS (-) spectra.

SPLAT measurement of m/z = 30 as a function of $[NO_2]$

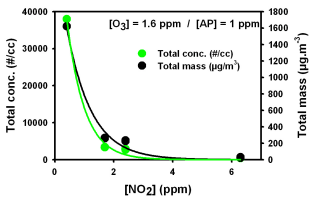


SPLAT MS spectra of 300 nm particles

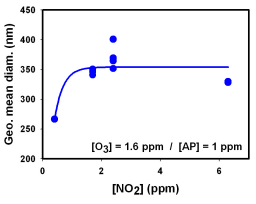


- m/z = 30 is the only marker fragment from nitrogen containing species in the SPLAT II-MS spectra. Its intensity slowly decreased with decreasing $[NO_2]$, indicating that the NO_3 initiated radical is still the dominant oxidation process.

Particle # concentration as a function of $[NO_2]$



Particle diameter as a function of $[NO_2]$



- Physical properties of the particles changed as illustrated by SMPS measurement of the particles as a function of $[NO_2]$.

CONCLUSIONS

- Data show that up to 7 different organic nitrates were formed in the NO_3 radical-initiated oxidation of α-pinene, as well as some other organic compounds.
- It is the first time that specific organic nitrates have been identified in particles.
- $[NO_2]/[O_3]$ ratio study shows a transition from NO_3 radical to O_3 initiated chemistry with the formation of less volatile species and a change in the particle properties.

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REFERENCES

1. Calogirou et al., *Atmos. Environ.*, 1999, 33, 1423-1439
2. Bonn and Moortgat, *Atmos. Chem. Phys.*, 2002, 2, 183-196
3. Hallquist et al., *Environ. Sci. Technol.*, 1999, 33, 553-559
4. Wängberg et al., *Environ. Sci. Technol.*, 1997, 31, 2130-2135
5. Alfarra et al., *Atmos. Chem. Phys.*, 2004, 6, 5279-5293
6. Pankow and Asher, *Atmos. Chem. Phys.*, 2008, 8, 2773-2796
7. Winterhalter et al., *Atmos. Chem. Phys. Discuss.*, 2003, 3, 1-39
8. Jaoui et al., *EST*, 2005, 39, 5661-5673